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14. ABSTRACT

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Block 13: Supplementary Note

An Ultrafast Look at Au Nanoclusters

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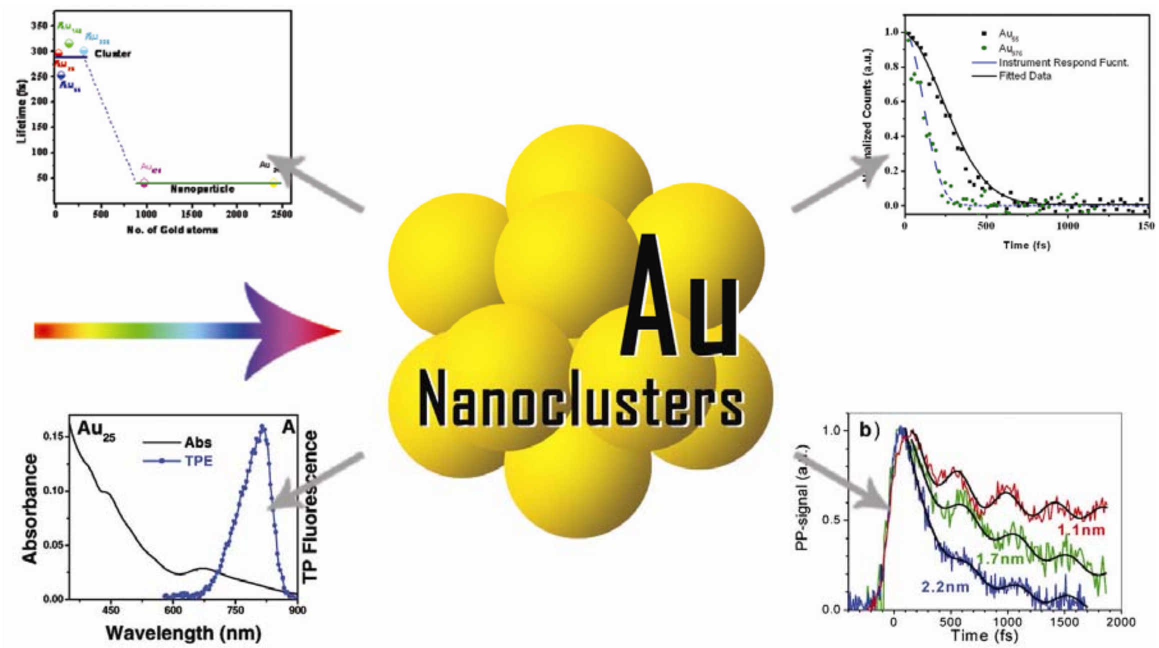
Conspectus

The area of research involving nano-materials in the past 20 years is credited with the discovery of many new and interesting properties not found in bulk materials. Extensive research has focused on metal nanoparticles (> 3 nm) because of their useful applications. The discovery of metal nanoclusters (<3nm) has greatly expanded the horizon of nano-material research. These nanosystems exhibit molecular-like characteristics as their size approaches the Fermi-wavelength of an electron. The relationships between size and physical properties for nanomaterials are very interesting. Particularly, the changes in the optical properties have provided tremendous insight into the electronic structure of nanoclusters. The success of synthesizing monolayer protected clusters (MPCs) in the condensed phase has allowed scientists to probe the metal core directly. Au MPCs have become the "gold" standard in nanocluster science, thanks to the rigorous structural characterization already accomplished. The use of ultrafast laser spectroscopy on MPCs in solution provides the benefit of directly studying the chemical dynamics of metal nanoclusters (core), and their non-linear optical properties.

In this contribution, the optical properties of MPCs in the visible region are investigated using ultrafast spectroscopy. An emission mechanism for nanoclusters is proposed based on fluorescence up-conversion. Nanoclusters behave differently from nanoparticles in terms of emission life-times as well as two-photon cross-sections. Further investigation of the transient (excited state) absorption has revealed many unique phenomena of nanoclusters such as quantum confinement effects and vibrational breathing modes. In summary, based on the differences in the optical properties, the distinction between nanoclusters and nanoparticles appear at a size near ~2.2nm. This is consistent with simulations from a free-electron model proposed for MPCs. The use of ultrafast techniques on these nanoclusters can answer many of the fundamental questions about the nature of these exciting nano-materials and their applications.



I. Introduction

In the past 10 years, nanoscopic materials have elucidated new frontiers in science, medicine and engineering. The development of new types of nanomaterials has lead to the discovery of metal nanoclusters which have gathered tremendous attention. Bulk metals are well-defined by classical dielectrics,[1,2] and are very well-understood. Recent studies on metal nanomaterials focus on systems comprised of a small group of metal atoms in the nanometer scale. Metal nanosystems have interesting physical properties, such as quantum confinement,[3–6] emission,[7,8] two-photon absorption[9] and other optical phenomena.[10,11] Extensive research in the past decade [6,12–14] initially focused on the synthesis of size-controlled metal systems; particularly those that approach the Fermi-wavelength of an electron. These metal nanosystems were classified as nanoparticles and nanoclusters. [6,14–17] It is interesting to note that for metal nanosystems in this size regime, the electronic properties are dictated by their sizes and shapes. The tunable size of metal nanosystems offers the possibility of a wide range of applications, including molecular electronics,[3–5,18,19] image markers[8,20] and catalysts[21].

Metal nanoparticles and nanoclusters are defined by their size. Nanoparticles have a metal core larger than about 3 nm, and nanoclusters smaller than about 3 nm.[6,7]

However with the exact divide between nanoparticles and nanoclusters are not clear until recently. The division of nanoclusters and nanoparticles arises from their drastically different optical properties.[7,9,16,17] Nanoparticles are already used in many fields, most notably in the field of imaging and extending the nano-tool box to an even smaller scale. Nanoclusters could provide an opportunity for an even wider array of potential applications. Metal topologies with a small number of atoms such as nanoparticles were first studied in the gas phase[22]. However, it was not until the condensed phase synthesis of metal nanomaterials that leads to tremendous interest experienced recently. The advancement of the synthesis processes also lead to an expansion of applications and, at the same time, the study of fundamental physics of these nanosystems.[6,10,14,15,18,23–28] Of the many different synthetic routes developed, Brust's synthesis[29,30] became a foundation for synthesis development, and is commonly used.[6,18] In brief, the synthesis uses an organic shell (Glutathione) to stabilize and regulate cluster formation from metal salt, creating highly stable metal systems. These systems were later labeled as monolayered protected clusters (MPCs). Using a straightforward "single-pot" synthesis strategy[31], Au(MPCs) can be synthesized with high stability[6,15,18,29,32], and receive much interest in the field. MPCs are considered to have two parts: a metal core and a single layer ligand shell.[15] The simple outer shell allows direct investigation of the metal core in the condense phase and it can be functionalized and adjusted to both polar and non-polar solvents.[13,33] The self-assembly nature of MPCs facilitates the synthesis of highly mono-dispersed products, and the metal core size can be adjusted by the reaction conditions.[6,15,29,31] The high purity (mono-disperse) and yield of MPCs synthesis allows for the accelerated characterization efforts.[7,18,34,35]

Detailed characterization work on Au nanoclusters leads to the identification of $Au_{25}(SG)_{18}$ [6,18,36–38] and various other species. One of the most definitive characterizations of Au MPCs is the x-ray crystal structure of $Au_{102}(SR)_{44}$[35] and $Au_{25}(SR)_{18}$.[6,10,38,39] The identification of $Au_{25}(SG)_{18}$ also coincides with theoretical work done on Au_{25}[39], giving further evidence to the structural details of the system. Theoretical works on Au_{25} gave insight into the bonding motif and the electronic structure of Au_{25}.[10,15,27,28,39–42] This account focuses on various optical phenomena observed for Au MPCs. Utilizing different ultrafast spectroscopic techniques, we are able to study the chemical dynamics of these

systems in great detail. Our investigations target the emission properties and mechanisms, non-linear optical responses, as well as transient absorption properties. The goal is to understand the fundamental scientific questions behind nanoclusters, such as the effect of size on optical behavior and the investigation of new optical behavior to further the understanding of nanomaterials in general and to advance the development of these new materials.

A. Electronic Absorption and Structure of Gold Clusters

The structure of metal nanoparticles and their electronic and optical properties are directly related, so it is important to understand the structure of MPCs for our discussion. The characterization of various MPCs leads to the discovery of "magic numbers":[32,43] similar to metal nanoparticles in the gas phase,[22] only metal core with certain sizes are found for MPCs. These magic number nanoclusters exhibit high stability and similar optical and physical properties, and can be modeled based on physical packing.[24] The stability of the larger nanoparticles can be well explained by the physical packing of the core. However, physical packing alone cannot account for the various sizes observed and leads to the development of the "super atom" theory.[15] The super atom theory adopts ideas from semi-conductors and treats the metal core as a single atom within the system. The highly stable cluster numbers are the result of the systematic closing of outer electronic shells, similar to the Jellium and Kubo models.[2,22] The simplest unit of Au MPCs was identified to be a 13 atom icosahedral core[34,37,38] and some of the magic clusters are found to be based on the same motif (physical packing or electron shell closing). It should be noted that Au_{102} does not follow the iscosahedral packing, but it does follow the electronic shell closing regime.[35] Most of the MPCs share a fundamental unit (Au_{13}), and in theory, should exhibit very similar physical properties. The treatment of the metal core as a super atom also gives rise to the idea of discrete (molecular like) energy levels for metal nanoclusters. Beside the super atom theory, the free electron model[6] can also be used to describe nanoclusters.

The direct effect of core size on the electronic structure for nanoclusters is known as the Quantum Size Effect. Our detailed investigations used various optical techniques to investigate the quantum size effect for Au MPCs and found that major optical difference can be observed between nanoparticles and nanoclusters at around 2.2-3 nm, in agreement with the free electron model. Moreover, nanoparticles were found to be similar to bulk metals and could be described by Mie theory.[1,7,44] Mie Theory utilizes Maxwell's equation to describe light interaction with metal nanoparticles and accounts for the Surface Plasmon Resonance (SPR). SPR is the collective excitation mode of the conduction electrons in the metal core, and it has been shown that enhanced emission from metal nanoparticles is caused by the SPR.[16,20,21] Control of the size and shape can directly affect the SPR, making nanoparticles a tunable image marker.[20] A comparison of the various steady state absorption spectra in figure 1 indicates the difference between nanoclusters and nanoparticles. The SPR is only observed for the nanoparticle, Au_{2406}. Based on Mie theory, [1,7,44] a simple model is used to simulate the absorption spectrum for a gold nanoparticle similar in size to Au_{25}. However, the calculation predicts the appearance of a surface plasmon band that can be observed at 520 nm, which is not observed in the experiments. This demonstrates that Mie theory (and its extensions),[1,2,44–46] does not apply to nanoclusters.

It is reported that absorption peaks for Au_{25} are correlated to the icosahedra structure of the core, and can be correlated to the transient absorption spectrum.[15,25,27,34]In our transient absorption spectra, we observed an additional absorption feature that we proposed to be related to the ground state.[7] The details will be discussed in the transient absorption section. In an attempt to resolve more details from the absorption spectrum, the Ramakrishna group[11] looked at the absorption spectra for Au_{25} and Au_{38} systems at low temperatures and observed a change in the absorption maximum, peak sharpening and an increase in the oscillator strength. Their model attributes the effect of the electron-phonon interaction with phonons in the metal-ligand interface.[11] Overall the absorption spectra of various Au nanoclusters and particles are clear evidence for quantum size effects.

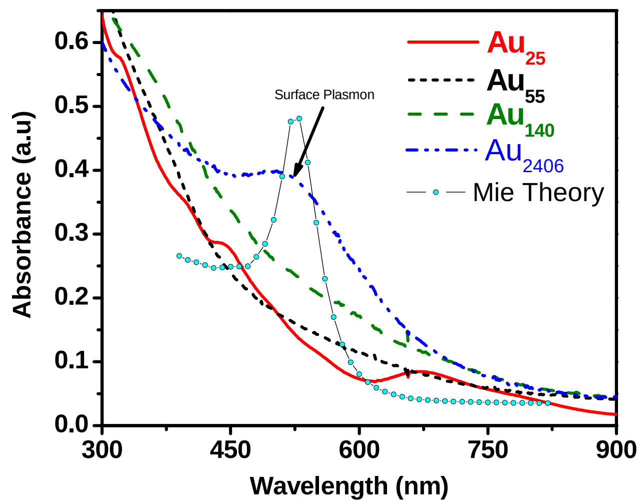


Figure 1: Steady state absorption for Au_{25} Au_{55}, Au_{140}, Au_{2406} and Mie theory calculation using parameter similar to Au_{25}.[7]

B. Emission Mechanism of Gold Clusters

Quantum confinement effects clearly predict discrete energy levels within the nanoclusters systems, and it is theoretically possible to observe emission.[2,7,15] Emission from MPCs was initially affronted with skepticism, due to the uncertainty in the purity of the materials and less-than-satisfactory characterization. Studies were carried out to look at the contribution from the ligand shell and the metal core separately, and it was found that neither component contributes to the emission.[47,48] In our contribution, one–photon excitation was used to observe two different emission wavelengths in the steady state, confirmed by time-resolved kinetics.[7] The emission is found to be in the visible and the near-infrared region.[7,8,45,48] It is relatively strong in the near-infrared with quantum efficiency on the order of 10^{-4}. The visible emission is weaker in comparison, with an efficiency of 1.25 $x10^{-5}$.[7] Quantum efficiencies at both wavelengths are five orders of magnitude stronger than that of bulk gold (gold thin films).[7]

To understand the emission mechanism better, time-resolved fluorescence up-conversion is used to resolve the fluorescence life-time of various gold nanoparticles and nanoclusters (Figure 2,3).[7,9] A femto-second Ti-sapphire laser system is used to achieve this goal with a time resolution of ~60 fs. The comparison of the fluorescence life-time of

nanoclusters and nanoparticles from 1.1 nm to 4 nm yields interesting results (Figure 2). There is a clear distinction between the emission life-times of nanoparticles and nanoclusters. In our previous investigation,[16] emission from nanoparticles is associated with the recombination of the *d*-hole by an Auger type process, which has a short life-time of 50 fs (Figure 3). The emission life-time for nanoclusters, however, is much longer than that of nanoparticles and can be fitted with a single exponential, which is characteristic of molecular-like singlet decay relaxation process.[7] (Figure 2, 3) The longer life-times are caused by the transition of discrete energy levels, similar to molecular emissions.

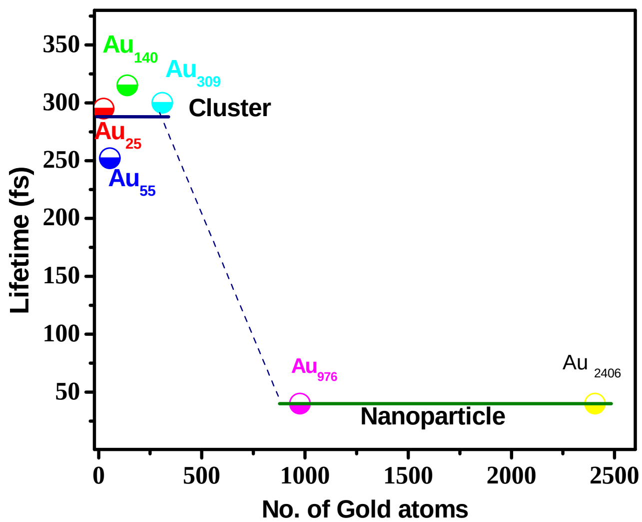


Figure 2: Fluorescence life time comparisons for MPCs of various sizes. The most notable difference is between the nanoparticle and nanoclusters.[7]

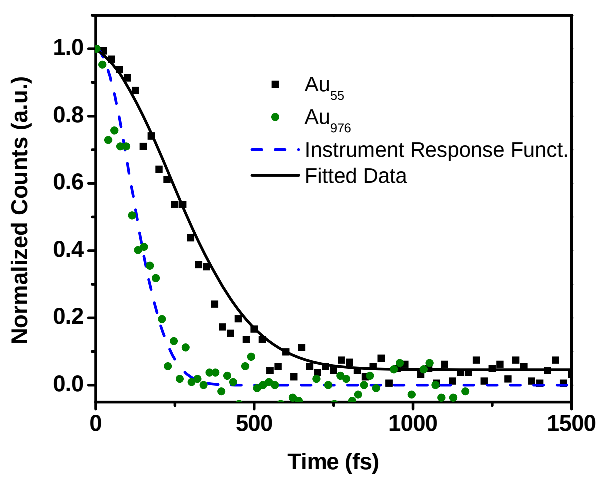


Figure 3: Time resolved visible emission for Au_{55} and Au_{976}. The life time of Au55 is about ~250fs. The emission from Au_{976} is faster than the instrument response function (blue line).[7]

Based on our steady state and fluorescence life-time studies, we proposed an energy diagram for nanoclusters (Figure 4). The emission studies[7] suggest that the dual-wavelength emission from Au MPCs follows two very different mechanisms. The emission in the visible region is fast and very short-lived (hundreds of fs), and it is most likely to be associated with the metal core (State B).[7,17] The near-infrared emission is related to the surface states that arise from the interaction with the ligands.[8,15,48]It has been reported that the polarity of the ligand has a direct effect on the emission efficiency.[6,48] In MPCs, the metal core and the metal-ligands bonds do not contribute to the metal core, based on the super atom theory. When we treat the metal core as one "super atom", the ligands can cause a change in the environment that affects the electronic states of the core as a whole.

The up-conversion studies suggest that the short-lived visible emission originates from the filling of the ground state hole by an electron from the excited state (Figure 4, B band).[7] This mechanism, however, is very different from the Auger recombination process for nanoparticles with a much faster life-times.[16,44] Compared to theoretical studies of Au_{25} clusters, this transition is similar to the HOMO-LUMO+1 process.[10,15] The small quantum efficiency forecasts the presence of non-radiative processes. These processes are represented by the transition from A band (LUMO) to the ground state (HOMO). The near-infrared emission is the result of the transition from the surface states, which originates from the A band, to the ground state. The absence of dynamic Stokes shift in our experimental results suggests that the energy is quickly transferred to the surface state, leading to the strong near infrared (NIR) emission.[7,8,15,45,48]

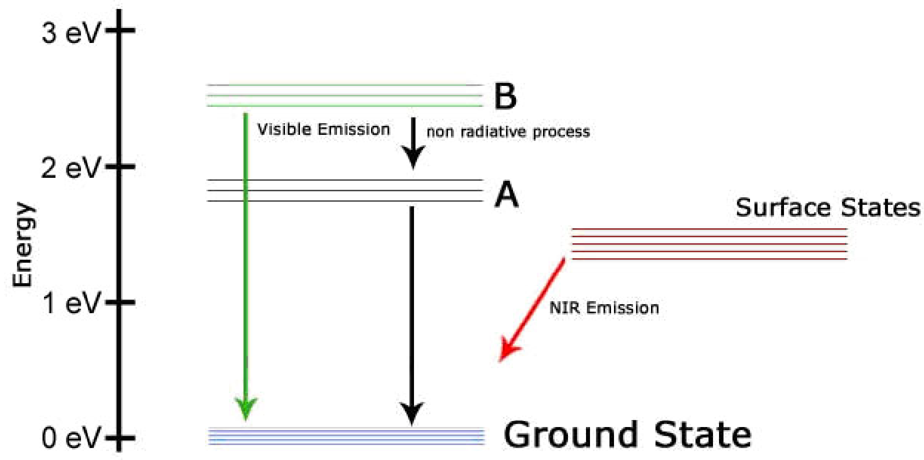


Figure 4: Transition energy diagram for the emissions for MPCs, using data from steady state emission, fluorescence up conversion and transient absorption.[7]

C. Two Photon Excited Emission in Gold Clusters

The relatively strong emission under single-photon excitation for Au MPCs leads to questions about the possibility of two-photon excited emission. Two-photon/multi photon excited emissions are beneficial for low power medical imaging. Au MPCs also have potential to be an optical limiting material with its large two-photon cross-section.[9] We expected to observe a scaling law for the two-photon absorption (TPA) coefficient as a function of the core size.[7,9] Two-photon excited emission was first with Au_{25} under 1290 nm excitation, with an emission peak at 830 nm (Figure 5a). The quadratic intensity dependence of the fluorescence indicates that it is a two-photon excited emission (Figure 5b). The TPA cross-section was measured to be 2700 GM using H_2TPP (Tetraphenylporphyrin) in toluene as a standard, about 1-2 orders of magnitude higher than many organic chromophores.[9]

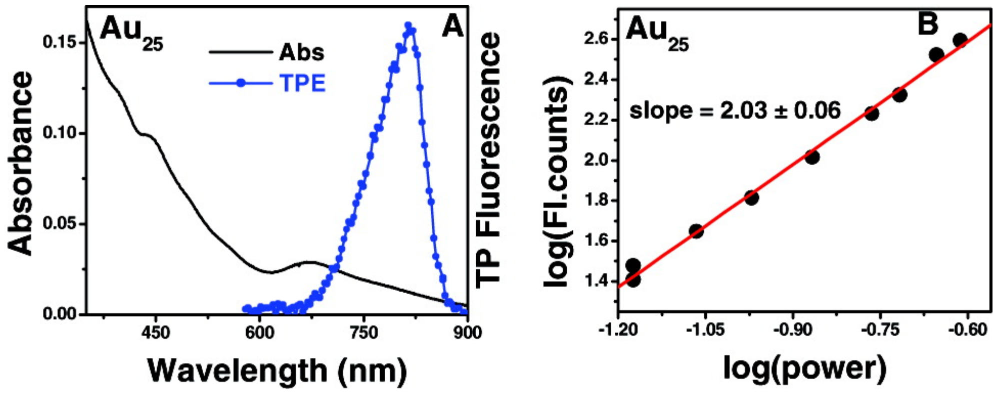


Figure 5. A) Two-photon excited fluorescence from Au_{25}. B) Pump power dependence for the two-photon excited emission.[9]

In addition to the two-photon emission in the near-infrared region, the emission in the visible region is also observed (Figure 6). Various sizes of Au MPCs are investigated, from gold nanoparticle (4 nm) down to Au_{25} clusters (1.1 nm), under 800 nm excitation. The emission wavelength maxima are found to have dependence on size for both nanoparticles and nanoclusters. For nanoclusters, the emission is in the 500-535 nm range, while nanoparticles emit around 550 nm. The difference in the emission wavelengths for the nanoclusters and nanoparticles is the result of the different energy gaps between HOMO and LUMO affected by the variation in size.[9] The fluorescence quantum yield under two-photon excitation is on the order of 10^{-7} to 10^{-8}. A clear illustration of the emission being a two-photon process is a quadratic power dependence of various clusters (Fig. 6b, d, f, h, j).[9]

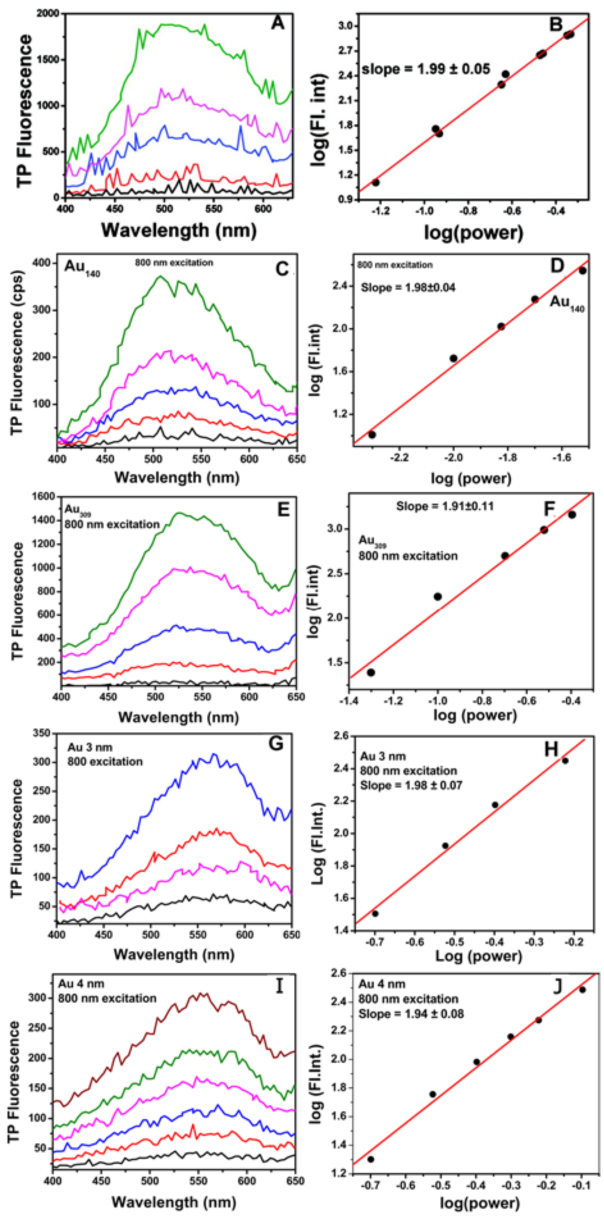


Figure 6. Two-photon excited emission and corresponding power dependence for MPCs of various sizes. A,C,E,G,I are the emission spectrum for Au_{25}, Au_{140}, Au_{309}, Au 3nm and Au 4nm respectively. B,D,F,H,J are corresponding power dependence.[9]

Due to the low quantum efficiency of these systems, measurement with a Spex-Fluorolog fluorimeter is difficult; two-photon excited femtosecond time-resolved fluorescence up-conversion[9] is employed to ensure accurate measurement of the TPA cross-section. The fluorescence kinetic decay traces for all gold clusters are measured with both one- and two-photon excitation. Using the ratio of the relative counts per

second at 100 fs time delay, the TPA cross-sections for all the gold clusters are determined. Absolute TPA cross-sections observed for the gold clusters are much larger than any of the experimentally investigated organic macromolecules or semiconductor nanocrystals.[9] The TPA cross-section for Au_{25} is 427,000 GM and Au_{309} 1,476,000 GM, much larger compared to a typical value of approximately 1000 GM at 800 nm for organic macromolecules. The large TPA cross-sections prophet the application of MPCs in optical power limiting, nanolithography, and multiphoton biological imaging. Comparisons of the two-photon cross sections of various MPCs also reveal scaling laws regarding core size and two-photon absorption cross-section (Figure 7a). There are two different trends, one for nanoclusters and the other nanoparticles. For nanoclusters, an increase in size is accompanied by an increase of the total two-photon cross-section. Nanoparticles Au_{976} and Au_{2406} follow a separate but similar trend. Analysis of the cross-section per atom (Figure 7b) reveals that the cross-section decreases with increasing cluster size. However, the correlation of size vs. cross-section is much smaller for nanoparticles.

Results from our fluorescence life-time measurements and two-photon cross-sections clearly demonstrate that there are differences between nanoclusters and nanoparticles. The distinction occurs at 2.2 nm. Au nanoclusters are a promising imaging tool because of their large two-photon cross-section. In addition, the lifetime and cross-section trends demonstrate the difference between the two nanosystems with a clear divide at about 2.2 nm, supporting the quantum size effect. The very large cross section for Au nanoclusters in the infrared IR spectral regions hold tremendous potential as an imaging tool, due to the fact that two-photon excitation in the IR region would allow for much deeper penetration into tissues with lower overall energy,[9,20] which is a very desirable trait for medical imaging.

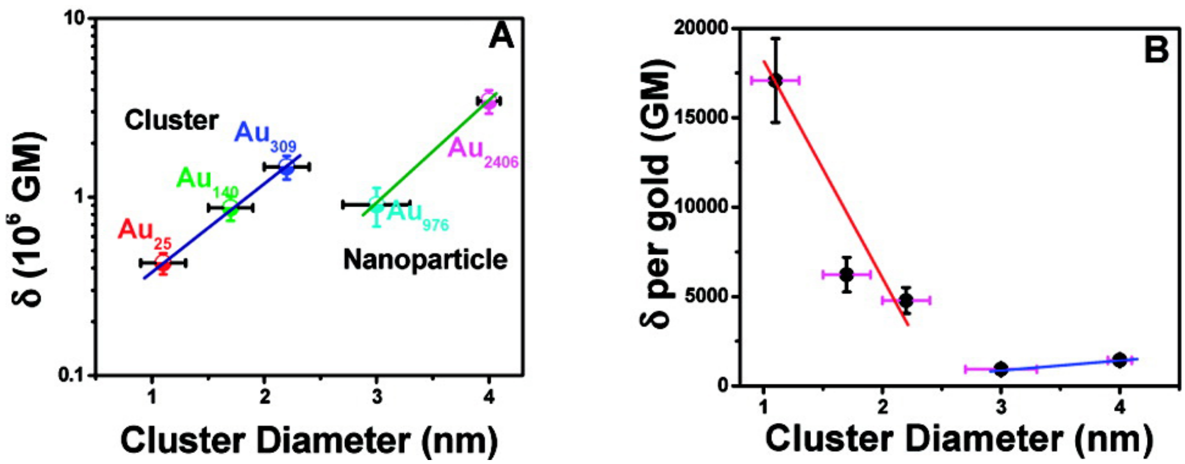


Figure 7. A) TPA cross sections for Au25 to Au2406 using two-photon excited fluorescence up-conversion. B) The TPA cross section calculated per atom. Red is for nanoclusters and blue is for nanoparticles.[9]

D. Transient Electronic Effects in Gold Nanoclusters

Transient absorption spectroscopy in the femtosecond scale allows for the study of energy states. The system is first excited by a pump pulse and the excited state absorption is measured by the probe pulse and compared to the ground state absorption. The transient absorption of nanoparticles and nanoclusters has been studied previously.[7,17,26,49,50] Our group focuses on the degenerate transient absorption (same wavelength pump and probe) as well as multi-color transient absorptions (450 nm – 750nm) of Au_{25}, Au_{55} and Au_{140} .[7,26] Transient absorption spectra of Au_{25}, Au_{55} and Au_{140} are compared at a time delay of 550 fs in figure 8.[7] The characteristic SPR at 530 nm is not observed for the three nanoclusters. Excited state absorption (ESA) occurs at 500 nm and 675 nm. The analysis of transient dynamics of Au_{25} nanoclusters with different charges (0,-1)[49] shows that the ESA signal near 670 nm can be bleached after 1 ns. This signal corresponds to the HOMO-LUMO transition in the Au core[7,26,27]. Comparison of the various Au nanoclusters emphasizes a positive correlation between the absorption and the core size, which we believe to be related to the quantum size effect.[7] The kinetic trace at 640 nm for Au_{55} (Figure 9) exhibits a quick initial relaxation to the intermediate state and then a slow decay back to the ground state. This decay profile is analogous to molecular-like systems with single electron relaxation processes.[7,16,507,16,55] Based on the work of Miller et al[26] and Qian et al[49], the observed dynamics of the nanoclusters suggest

a core-core HOMO-LUMO charge transfer (~1 ps) followed by a core-shell charge transfer (>1 ns).[49] However, the dynamics of the nanoparticles are very different from those associated with nanoclusters. Nanoparticles' transient signals follow Auger type kinetics, and the mechanism of relaxation is related to electron-phonon processes.[7,16,44]

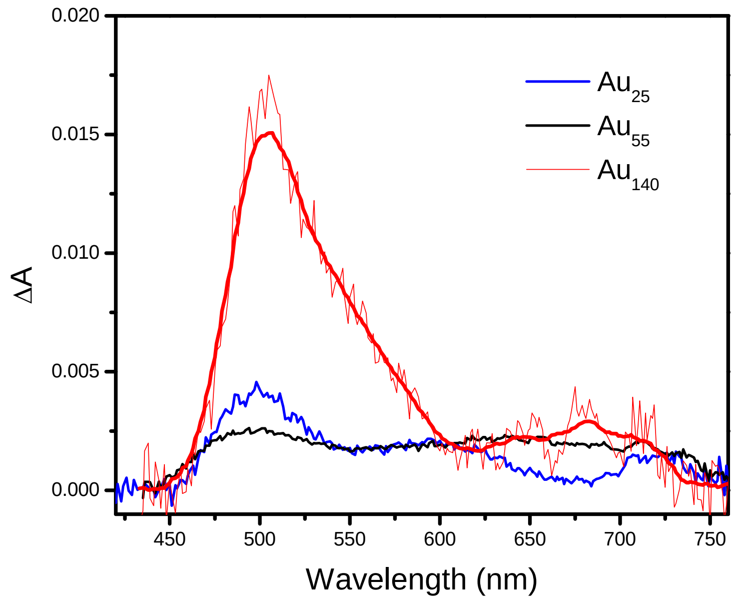


Figure 8: Transient absorption for Au_{25}, Au_{55} and Au_{140}, at 550 fs.[7]

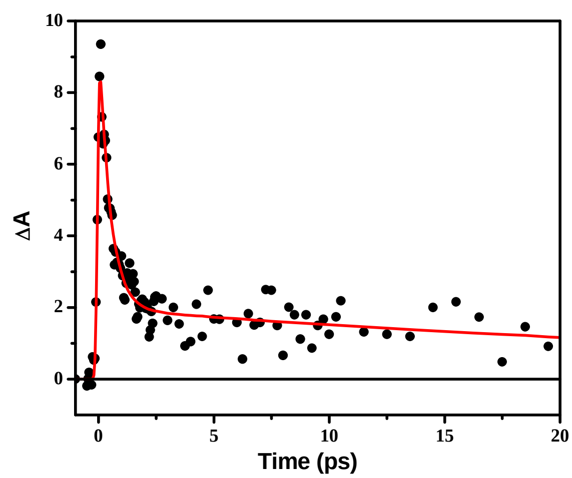


***Figure 9*:** The kinetic trace from transient absorption for Au_{55} at 640nm.[7]

Detailed analysis of the transient data also uncovers additional information about Au nanoclusters. The analysis of the transient absorption data in literature[7,26] showed that the

bleaching observed at ~670 nm corresponds to a HOMO-LUMO absorption peak and can be assigned to the ground state bleach. In our experiments, we observed an additional bleach near 550 nm (Figure 11,12). This can be correlated to the weak shoulder observed in the steady state absorption spectrum (Figure 12).[7] Using the same analysis, the bleach at 550 nm could be another ground state for the Au_{25} system.[7] In additional to the transient absorption comparison, the pump power dependence for Au_{55} is also investigated to probe electron-electron and electron-phonon relaxation processes.[7] Electron-electron scattering for the gold nanoparticles is attributed to the sharing of energy by excited electrons, followed by the thermal relaxation of the electronic gas [16,44] and is weakly power dependent.[7] Electron-phonon relaxation corresponds to the transfer of energy from electron system to the lattice.[16] Larger nanoparticles exhibit electron-phonon relaxations which depend strongly on pump power.[7] We do not observe these phenomena for nanoclusters because of their discrete energy levels (Figure 10).[7]

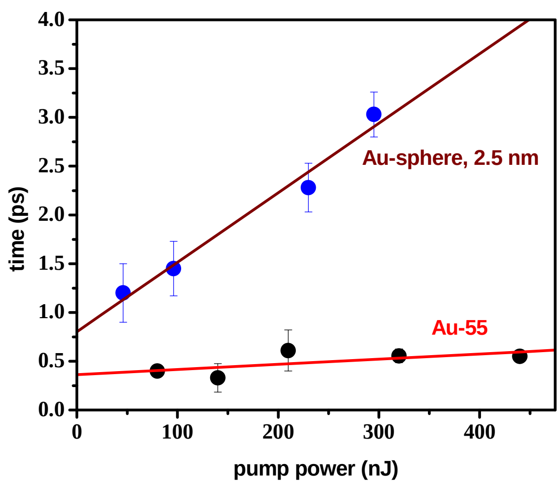


***Figure 10*:** Pump power dependence against average life time for 2.5nm nanoparticle and Au_{55} (1.4nm).[7]

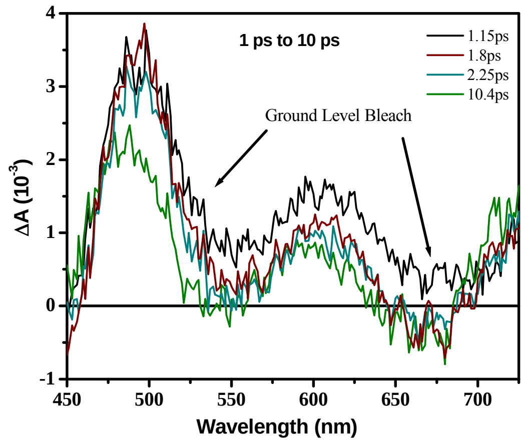


Figure 11: Transient absorption of Au_{25} in hexane, probed from 450nm to 750nm. Ground level bleach can be observed at 550 nm and 675 nm.[7]

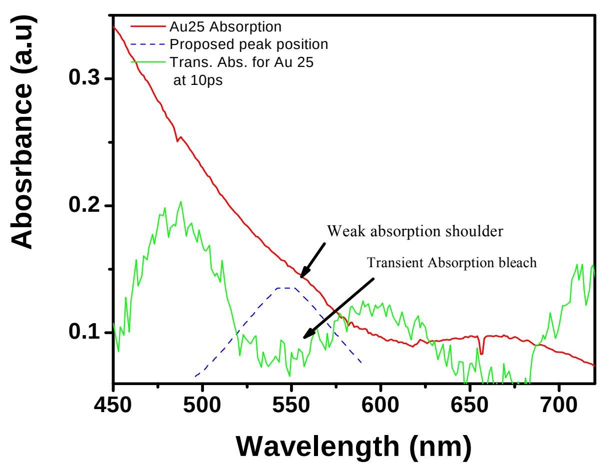


Figure 12: Steady state absorption compared to transient absorption for Au_{25}, with ground level bleach at 550 nm.[7]

Using degenerate pump-probe experiments, the excited state dynamics of the MPCs can be measured in a high time resolution.[7,50] Acoustic modes and their excitation characteristics in nanomaterials contain important information about the structure, geometry, and their interactions with the environment. The structural assignment of both Au_7 and Au_{20} in the gas phase is accomplished using vibrational spectroscopy, and it is also theoretically predicted that the nature of internal vibrational energy redistribution is a

key factor in promoting reactivity of small gold clusters.[51] For gold nanoclusters with polypeptide chains, vibration transfer in the THz range has been predicted using molecular dynamics simulations.[52] Coherently excited "breathing" vibrational modes for gold nanoparticles are proposed with a response time spanning from a few picoseconds to tens of picoseconds.[53–56] The breathing mode frequency is also inversely proportional to the particle size. The mechanism for such breathing mode in nanoparticles can be explained by the impulsive heating of the particle lattice after short pulse laser excitation.[53–55]

Our degenerate transient pump-probe[44,57] detected oscillations with a period of ~ 450 fs (2.2 THz),[50] which compares well to a low-frequency vibrational density of states theoretically calculated for gold clusters.[58,59] The fast oscillation period is similar to oscillatory features reported for Au_5 in femtosecond photoelectron spectroscopy experiment.[58] Based on the oscillatory period, the mechanism is different than nanoparticles and is more closely related to semiconductors and/or molecular systems.[60] Compare to the lack of oscillatory features for nanoparticles, the appearance of the oscillations for small MPCs can be correlated to the emergence of an optical energy gap near the Fermi level.[50] Au nanoclusters of various sizes were tested (Figure 13b) and showed frequency independent breathing mode. The lack of size correlation may be an indication that the oscillatory feature is a shared core phenomenon.

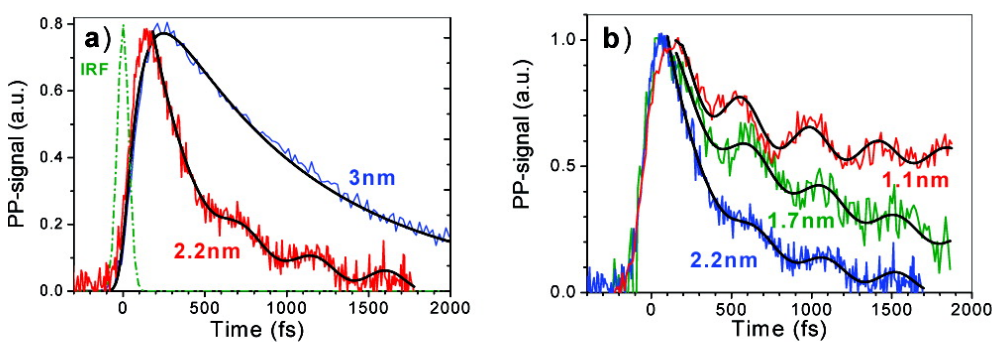


Figure 13: A) Degenerate pump-probe experiment on Au MPCs shows clear oscillatory features for nanoclusters. B) Comparison of oscillatory features of nanoclusters of various sizes.[50]

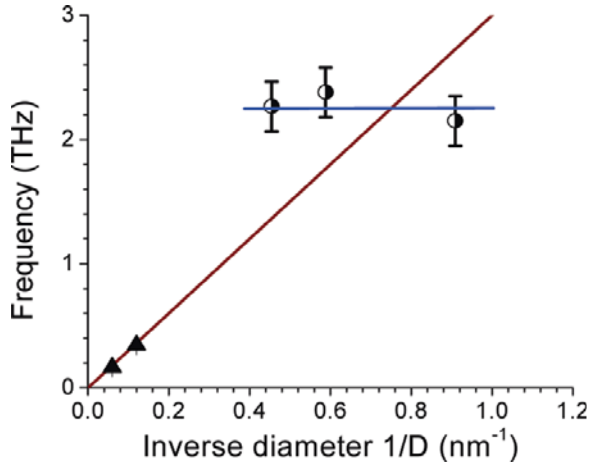


Figure 14: Acoustic vibration frequency size dependence. Solid triangles are frequencies of the "breathing" vibrational modes previously observed for larger gold particles. Solid brown line is the classical mechanic calculations for the elastic gold sphere. Horizontal blue solid line is a guide to the eye.[50]

Summary

Monolayered protected clusters have unique physical and optical properties. The steady state absorption and emission illustrated the quantum size effect of MPCs. The dual emission nature for MPCs confirmed the super atom nature of these materials. Based on various ultrafast spectroscopy techniques, different mechanisms were proposed to explain the visible and infrared emissions of MPCs. Time resolved florescence spectroscopy serves as proof for the weak emission in the visible region for Au_{55}. The quantum yields in the visible region are five orders of magnitude larger than that of bulk gold; this emission enhancement is due to the discrete energy levels in the metal core, not the SPR. Very large two photon cross-sections were observed for Au MPCs, which suggests future applications of MPCs as an optical limiting material. Experimental evidence indicated that the size distinction between nanoparticles and nanoclusters is ~2.2 nm. Transient absorptions results identified an additional ground state absorption that has not been observed previously. The vibrational breathing mode found in degenerate transient absorption shows no size dependence on the mode frequencies and could used in the characterization of nanoclusters. Overall, our optical studies yield many interesting results and also raised many more interesting questions. One of the biggest challenges ahead will be the refinement of unified laws (such as the super atom theory)

that govern all nanoclusters, and investigate in detail the relationship between the metal core and its environment. The field of MPCs is still at its infancy, with many application and fundamental science yet to be explored and we look forward to the new discoveries and opportunities ahead.

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Sung Hei Yau received his B.S in Chemistry from University of Michigan in 2003 and later returned to Michigan to pursue his Ph.D in Chemistry. Sung Hei met Professor Goodson during his undergraduate study and has been working closely with Professor Goodson ever since. Optical properties of nanoclusters have been a major focus of his work at Michigan using ultrafast systems. Sung Hei Yau received a Chemistry Research Excellence Awards fellowship from the Department of Chemistry, Best Paper Award at the 16th International Conference on Luminescence and a travel award at the Vaughan symposium.

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